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# MOLECULAR EMISSION SPECTRA FROM SHOCK-DECOMPOSED BENZENE

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## ABSTRACT

Benzene decomposes when shocked to pressures greater than 13 GPa; However, few products of the decomposition reactions have been identified in situ or by recovery methods. This paper reports the detection by time-resolved (50-to-120 nsec) chemiluminescence spectroscopy of excited molecular products of the decomposition of benzene at pressures from 24 to 63 GPa. Strong spectral bands characteristic of C<sub>2</sub> are readily identified among other features and a gray-body background. The dependence of the spectra on shock parameters are briefly discussed in terms of known decomposition mechanisms of highly excited benzene.

## INTRODUCTION

The extent to which chemistry occurs in the shocked state and, if so, may differ qualitatively from chemistry at the same static temperatures and pressures has been actively considered in the shock wave community.[1] Benzene is typical of many organic molecules that react at shock and static pressures of the order of 10 GPa and moderate to high temperatures. From analyses of recovered products, some investigators [2] have concluded that the shock-induced chemistry differs qualitatively from the chemistry produced by the combination of high static pressures and temperatures. However, the specific chemical reactions that benzene undergoes at high shock pressures are not known.

The work described in the paper represents the first detection of molecules formed immediately behind the shock front during shock compression of benzene at pressures from 24 to 63 GPa. C<sub>2</sub>, among other species, have been detected by their chemiluminescence, collected with 50-to-120-nsec resolution during passage of the shock front through the focus of an emission spectrographic system with gated diode-array

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detectors. In the following sections, the spectroscopic techniques used to detect these molecules are outlined, and typical spectra are described. The relevance of these observations to the known high temperature-low pressure [3-5 and references cited therein] and high static pressure chemistry of benzene [6-8] is discussed, and some directions for further work are suggested.

## EXPERIMENTAL

The experimental techniques are briefly outlined in this section. Special features of the optical system are emphasized since space limitations preclude a complete description of the apparatus. A more complete description of the sample holder, sample, and optics will be published elsewhere. [9] The shock techniques were similar to those used for optical pyrometry [10] and other optical studies of liquids. [11] Deoxygenated benzene samples (Mallinkrodt [12] analytical reagent grade) nominally at 295 K were confined in 32-mm diameter by 5-mm thick cylindrical cavities in Al targets, between Al base plates and quartz windows. Three self-shorting pins also were mounted in the benzene cavity and extended within 4.5 mm of the base plate. These pins detected the arrival of the shock and triggered (after appropriate electronic delays) the gated detectors.

Planar shock waves were generated by impacting the target with projectiles accelerated to velocities in the range 4-7 km/s. The velocities of the projectiles were measured by flash x-ray photography. Thermodynamic states in the samples were calculated by the shock impedance matching method from measured velocities (in the range 4-to-7 km/sec) of the metal impactors and published equations of state for the impactors, base plates, and benzene. [4, 21, 22]

The spectrometers had four major components: a quartz collection collimator; a mirror that diverted the optical path by 90° from the gun axis; a broadband beamsplitter; and 1 or 2 monochromators with gated intensified diode-array detectors. The collimators were focused inside the benzene, 0.5-mm along the cavity axis from the surface of the quartz window. For most of the experiments to date, 25-mm diameter f/4 fused quartz collimators were mounted inside the evacuated target chamber of the gas gun; but, for 3 experiments, the collimator was a 10-cm diameter f/10 quartz acromat, mounted outside the vacuum chamber. With the latter arrangement, the spectral response of the spectrometer could conveniently be calibrated with a standard 2800 K lamp.

At various times, two Spex 0.25-meter grating monochromators were used to analyze the spectra. One monochromator had a 300 groove/mm grating with a 1 micron blaze and a Princeton Instruments IRY/700 array detector; the second monochromator was equipped with a similar 300 groove/mm grating (or, for some experiments, a 600 groove/mm grating blazed for 500 nm) and a Tracor Northern array detector. Each detector could cover a 120-to-250 nm range of wavelengths. The gate durations and delays of the detectors were set so that: (a) the detectors collected radiation emitted for a 50 or 120-nsec period during which the shock front passed through the focus of the optical system and (b) the gates were off before the shock front arrived at the quartz window.

For the initial experiments, the slit widths and detector gains were set somewhat arbitrarily. Some spectra were much more or, rarely, less intense than the electronics could process accurately; and some intense features were cut off or detected with low resolution. Since the spectra were observed through unshocked benzene, wavelengths less than 270 nm

could not be detected. No attempt was made to separate overlapping second-order features at first-order wavelengths longer than 550 nm.

## RESULTS AND INTERPRETATION

Fig. 1 shows 9 spectra from 7 shock experiments at pressures from 24 to 63 GPa. These plots have not been corrected for the spectral responses of the optical systems; but comparison of this plot with the corrected plot of spectrum f in Fig. 2 implies that these corrections are relatively minor. In addition to broad gray-body backgrounds that become more intense with increasing pressure, several molecular features are apparent in these spectra. The violet-shaded bands whose red edges are near 470, 515, 550, and, in many spectra, 610 nm are the  $v''=v'+1$ ,  $v''=v'$ ,  $v''=v'-1$ , and  $v''=v'-2$  bands the Swan A  $^3\Pi_g \rightarrow X^3\Pi_u$  system of  $C_2$ . [13] Each band broadens toward higher wavelengths with increasing pressure as a result of emission from higher  $v''$  levels that, as one might expect, are more highly populated as the pressure, energy, and temperature behind the shock front increase.

The intensities of the bands are determined by competition among rates at which  $C_2$  forms, radiates, decomposes, and is quenched and rates

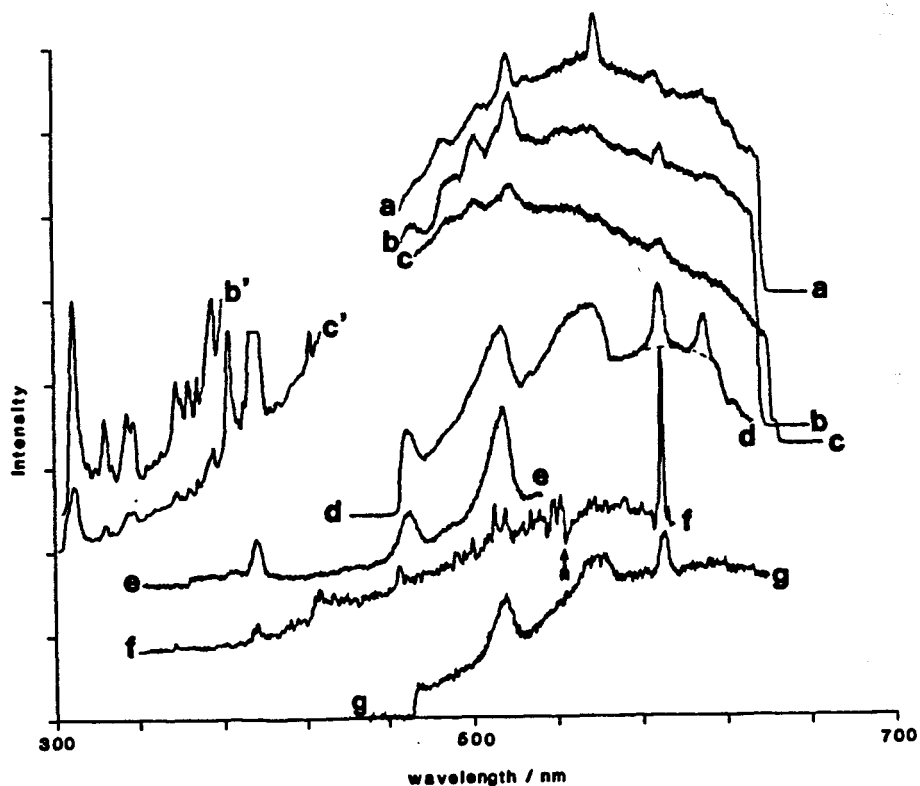


Fig. 1. Tribochemiluminescence of benzene shocked to: a, 63; b-b', 58; c-c', 59; d, 50; e, 38; f, 29; and g, 24 GPa. Except for f, f/4 lenses, the Princeton Instruments detector, and 5-nm instrumental resolution were used to collect the spectra. For clarity, the dark levels of these spectra (indicated by data from a few unintensified diodes); and the intensities have been multiplied by: a, 5; b, 1; c, 1; d, 5; e, 25; and g, 34. Spectra b', c', and f were obtained with the Tracor Northern detector at about 1-nm resolution. The dip above the arrow in spectrum f is an artefact.

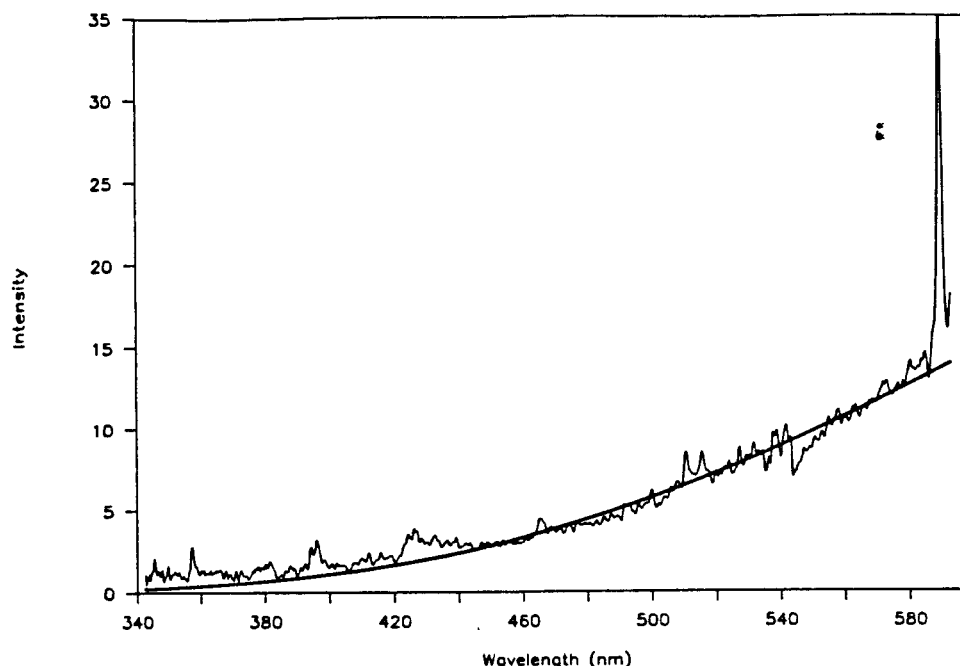


Figure 2. Spectrum f of Fig. 1, corrected for the spectral response of the optical system, is compared with a smooth 2250 K black-body spectrum.

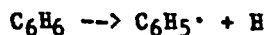
of other processes behind the shock front. Thus, intensities are not quantitatively equivalent to populations. However, the fact that, relative to the gray-body spectra collected with the same optics, the Swan bands are most intense at 38 GPa suggest that the yield of  $C_2$  is highest near this pressure. The molecular bands also appeared to be weaker (relative to the gray-body continuum) in the 3 spectra obtained with f/10 optics, including spectrum f. The f/10 optics have a greater depth of field, and the lower intensities of the molecular spectra may mean that the emitting molecules are in a relatively thin zone between the shock front and a zone of highly emissive material that produces the grey-body spectrum.

Another common feature of many spectra is the band near 395 nm of e in Fig. 1. In b' and c', this band saturates the detector, while it appears as two lines at 394.4 and 396.2 nm in f. Although possible changes of the wavelengths and shapes of spectra with pressure make it difficult to assign this band unambiguously. One possible assignment is as the 390-nm  $B \rightarrow X$  system of CH. [13] If CH were present, the broad band near 430 nm in f, part of which also may be seen in spectrum c', may be part of the  $A^2\Delta \rightarrow X^2\Pi$  system. [13]. The 430-nm system, however, usually is the stronger of the two CH bands in flame spectra, although in special situations their relative intensities may be reversed. [14] Since these CH bands terminate in molecular ground states, this assignment might be tested in future experiments by attempting to detect laser-induced fluorescence from the shock front.

The persistent feature at 588 nm may be the yellow Na line, but a 294-nm band in second-order among other possibilities have not been excluded. Other features of these spectra have not been identified with known molecular emission bands. Promising coincidences with some uv features can be inferred from absorption spectra reported for species such as  $C_2H$  [15] and  $C_4H$  [16] and might be tested by laser-induced fluorescence.

The smooth curve in Fig. 2 represents the fit of a  $2.25 \times 10^2$ -K black-body spectrum to the corrected 29-GPa spectrum. Similarly good fits to gray-body spectra obtained at 29 and 42 GPa were obtained with black-body spectra for  $2.6$  and  $3.4 \times 10^2$  K, respectively. These temperatures are in good agreement with the "reactive high  $C_p$ " fit to 5-channel pyrometry of shocked benzene reported by Nellis et al. [10]. Thus, it is likely that the observations described in this paper were obtained at temperatures and pressures between about 2000 K near 20 GPa and 4800 K near 60 GPa. Extrapolation of this "reactive high  $C_p$ " fit to 13 GPa indicates that the temperature behind the shock front at this "transformation" pressure is  $1350 \pm 150$  K.

The rapid formation of  $C_2$  and other products of ring-opening chemistry behind the shock front and the 13 GPa transition pressure then can be understood in terms of what is known about benzene pyrolysis at lower pressures. This chemistry has been discussed in recent publications by Kiefer et al. [3] and by Smith and Johnson [4] among others. When benzene is pyrolyzed in shock tubes and flow reactors at pressures of the order of  $10^5$  Pa and temperatures below about 1300 K, polyphenyls are the major products. These products are formed by scission of C-H bonds on the benzenes to form phenyl radicals:



and subsequent free radical propagation and recombination reactions. This accounts for the often cited "expectation" that the products of benzene shock chemistry should be aromatic. However, when benzene is pyrolyzed occurs above 1300 K at low pressures, reactions that open the phenyl rings, for example:



predominate over the free radical reactions.  $C_2H_2$  is the major product; but large amounts of  $H_2$ ,  $C_4H_2$ , higher polyacetylenes, and carbons are also produced by a complex series of reactions within micro- to milli-seconds. [2, 3, 5]

The rates of many of the reactions involved in benzene pyrolysis are reported to vary strongly with both pressure and temperature, with many of the reactions going more rapidly at higher pressures. Thus, it is not surprising that reactions, which occur in the milliseconds or microseconds near atmospheric pressure, proceed in nanoseconds at pressures 5 orders of magnitude higher nor that the "transformation" of product yields from aromatics to acyclics on the shorter time scale characteristic of high pressure shocks occurs near the same temperature of the low-pressure transformation.

#### SUMMARY

Emission spectra characteristic of excited  $C_2$  and other small molecules generated by shock-induced pyrolysis of benzene at pressures from 24 to 63 GPa have been detected from a thin zone behind the shock. The species are similar to molecules found on the milli- to micro-second time scales in pyrolysis at comparable temperatures at low pressures. It, thus, appears that chemistry in the two pressure regimes is similar; but, not surprisingly, rates differ. These rapid detection techniques, and extensions involving various laser-induced spectroscopies, may help to elucidate mechanisms of other fast reactions at high shock pressures.

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